On Fine Management of Fuel Composition in Molten Salt Reactors

Pavel N. Alekseev[1], Alexander L. Shimkevich[2]

[1,2] NRC Kurchatov Institute 1, Kurchatov Sq., Moscow, Russia
[1]apn@dhtp.kiae.ru; [2]shall@dhtp.kiae.ru

Abstract- **A concept for precise controlling and fine managing a fuel composition of molten-salt reactor (MSR) is formulated for maintenance of given properties, low corrosion activity and extremely selective extraction of metal component from the molten salt. A possible application of a potentiometer and a method of columbic titration of basic-metal atoms through galvanic cell on solid electrolyte with cationic conductivity, for example, $Na^+-\beta''-Al_2O_3$ is discussed for monitoring and varying the RedOx-potential of MSR fuel compositions.**

Keywords- Molten-salt Reactor; Fuel Composition; RedOx-potential; Precise Controllin and Fine Managing; Galvanic Cell with Solid Electrolyte

I. INTRODUCTION

Despite of wide experience at using molten salts in reactor technologies [1], there is no attention called for studying their electronic structure, not to mention the influence of non-stoichiometric salts or their reduction-oxidation (RedOx) potential on structural, thermodynamic, physical and chemical, kinetic and corrosion properties of liquid salts.

As the RedOx–potential, they understand a thermodynamic potential, $-\Delta G_X$, of common metalloid, X, for all components of molten-salt mixture, $\sum_{i=1}^{n}(M_iX_{k_i})_{\alpha_i}$ [2-4], expressed by

$$-\Delta G_X = -\Delta G_o[\sum_{i=1}^{n}(M_iX_{k_i})_{\alpha_i}] + RT \ln a_X. \qquad (1)$$

Here $-\Delta G_o$ is the standard potential of molten-salt mixture; $M_iX_{k_i}$ is the molten-salt component of variable composition: $k_i = k_i^o \pm \Delta k_i$ where k_i^o is the stoichiometry coefficient; a_X is the thermodynamic activity of common metalloid in liquid mixture of salts; R is the gaseous constant; T is Kelvin's temperature.

The investigation of electronic structure of molten salts can be useful for proving choosing their fuel composition in molten-salt reactors (MSR), for developing its operation technology, fine and controlled separation of fission products, the minimal corrosion of structural materials, i.e. it will allow to prove designing the fuel compositions and reliable operation of molten-salt mixture in non-isothermal conditions of MSR [5].

In this work, two methods are considered for precise (potentiometer) monitoring and fine controlling the RedOx–

potential by the columbic titration of metal atoms through a solid membrane with unipolar conductivity of sodium (lithium) cations for the fuel compositions containing alkali salts. These methods are metrological determined against to up-to-date current-mode monitoring the RedOx–potential of molten salts, working as non-equilibrium indicators and consequently demanding their permanent calibration. The offered methods allow not only to supervise this parameter with high accuracy (±5 mV), but also to hold it at the given level with the same accuracy by fine and reversible dosing the basic metal of molten-salt mix. We will consider in details this concept by the example of chlorides in the eutectic melt of a LiCl–KCl system.

II. CONCEPT FOR FINE EXTRACTING METALS FROM MOLTEN SALTS

It is possible [6] to measure precisely the reduction potentials of actinides and lanthanides in the LiCl–KCl eutectics for different electrodes (see Fig. 1) due to well measured equilibrium pressure of the gaseous chlorine with its chemical activity (their RedOx–potential) in molten chlorides.
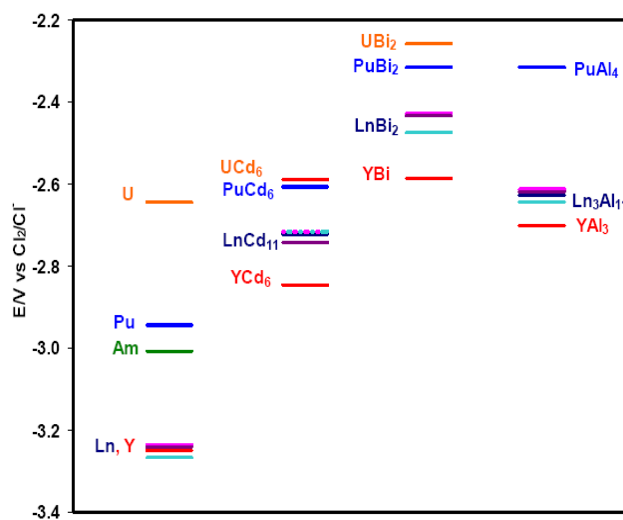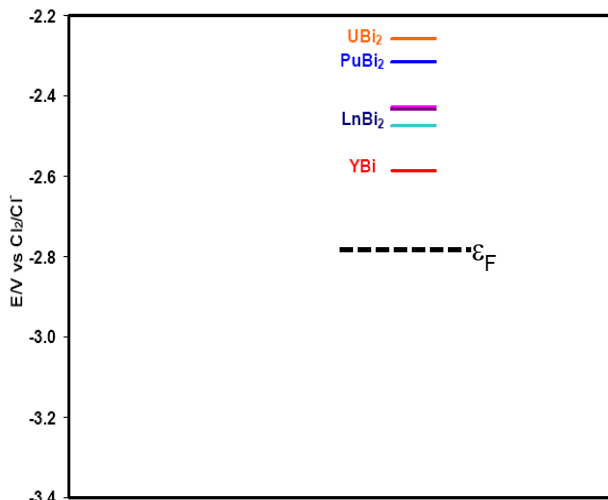

Fig. 1 The reduction potentials of actinides An(III)/An(0) and lanthanides Ln(III)/Ln(0) in LiCl–KCl eutectics for different cathodes from right to left: solid and neutral, liquid cadmium and bismuth, and solid aluminum at 723 K provided by $x_M(salt) = x_M(Cd) = x_M(Bi) = 0.001$ [6]

It is visible that these potentials depend on the cathode type and they are determined for equal portions of added atoms in the salt and cathode (special case). It is important to note that these potentials differ from each other by 10–

100 mV. This gap will be probably enough for extracting (deeply and selectively) needed radio nuclides from the MSR molten salt in holding an over voltage of the galvanic cell at the same level.

In clarifying the concept for fine extracting the dissolved metal impurities from molten-salt compositions, it is possible to consider as analogue the LiCl–KCl eutectics in contact with liquid bismuth (see Fig. 2). It is visible that Fermi's level, ε_F, (RedOx–potential) is necessary to measure with accuracy not worse ± 5 mV in a range of extraction of the shown impurities because the electronic levels of impurity components lay densely in a band gap of the molten salt. Such the accuracy can be provided only by e.m.f. method on solid electrolyte of $Li^+-\beta''-Al_2O_3$ [4].

(a)
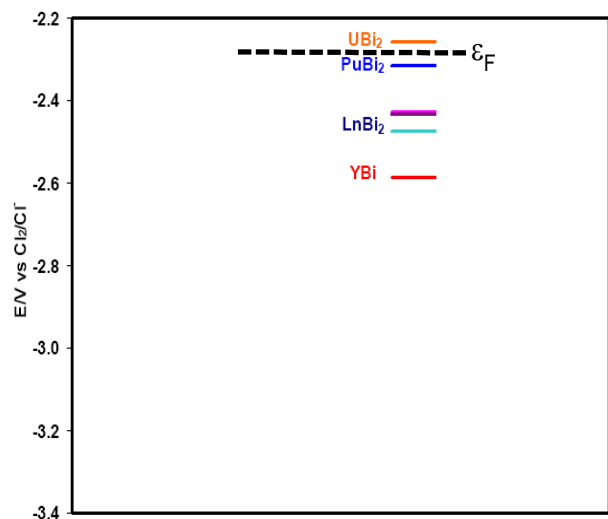
(b)

Fig. 2 The reduction potentials of actinides An(III)/An(0) and lanthanides Ln(III)/Ln(0) in LiCl–KCl eutectics for liquid bismuth at 723 K provided by $x_M(salt) = x_M(Bi) = 0.001$; dotted lines designate Fermi's level, ε_F, corresponding to different values of the eutectics RedOx–potential

It is known [7] that the current polarization of the galvanic-cell electrodes can lead to appreciable deformation of the allowed states of electrons in the molten-salt band gap directly near electrodes so that one of the basic-metal components in salt composition (K or Li in this case) can be extracted from the molten salt together with impurities. Therefore the control of RedOx–potential of salts (monitoring and managing the thermodynamic activity of lithium or other base metal) should be carried out with the help of electrochemical cell on solid electrolyte working at the fixed and precisely measured over voltage but not at the fixed current mode [4].

The Fig. 2a shows the level of molten-salt RedOx-potential when the marked impurities cannot be removed from the salt solution in general and the Fig. 2b shows the one at that level when all the marked metal impurities (except uranium) are removed from the salt solution.

In observed closeness of these levels as allowed energy states of electrons, the extraction of corresponding impurities can be carried out only at the low over voltage, $\Delta E \le 10$ mV, of galvanic cell. At the same time, the levels of their potentials are to be measured as stated above with high accuracy and in a wide range of temperatures. It is possible to realize only by e.m.f. method with the help of potentiometer of basic metal component, for example, lithium.

III. MONITORING THE REDOX–POTENTIAL

For the precise control of the molten-salt reduction–oxidation potential, one should use the electrochemical gauge of thermodynamic activity of the basic-metal component (for example, Li or Na) work upon base of solid electrolyte with unipolar conductivity of its cation. Then, it will generate e.m.f. determined by Nernst's equation [4].

$$E = -(RT/F) \ln a_M, \qquad (2)$$

where E is the e.m.f. of galvanic cell; F is the Faraday's constant; a_M is the thermodynamic activity of basic metal in molten salts.

Such membrane can be made from $Na^+(Li^+)-\beta''-Al_2O_3$ which provides univocal correspondence of the e.m.f. generated in it with the thermodynamic activity of sodium (lithium) in the liquid electrode if a reference electrode is the pure liquid sodium (lithium) [8].

In order to use the solid membrane of $Na^+(Li^+) - \beta''-Al_2O_3$ as the sensor of thermodynamic activity of sodium (lithium) in liquid salts, it is necessary to exclude a direct contact of the solid electrolyte and the molten salt, simultaneously providing an effective exchange of the sensor and liquid salt by atoms of sodium (lithium). Such technical problem is being solved at intercepting the material of $Na^+(Li^+)-\beta''-Al_2O_3$ and the molten salt by a liquid-metal measuring electrode (for example, of lead or bismuth) as a layer in a felt of thickness less than 0.1 mm [8]. The schematic diagram of such gauge is shown in Fig. 3.
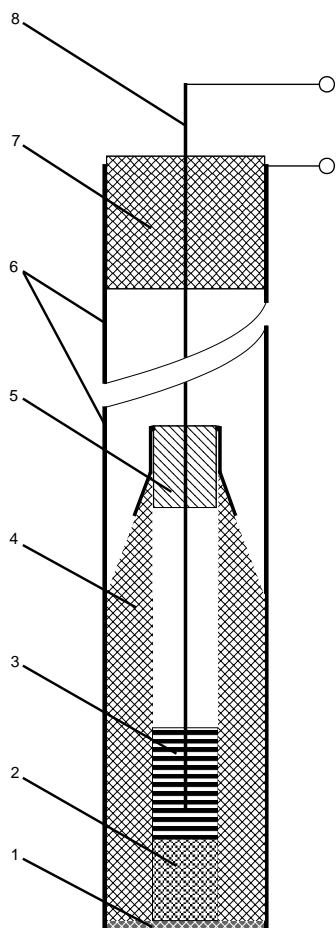
Fig. 3 The schematic diagram of the gauge of sodium for monitoring the RedOx–potential of molten salt including the liquid-metal measuring electrode 1, the cylindrical plug of solid electrolyte 2, reference electrode of liquid sodium 3, the electro isolating bush 4, the seat 5, the metal covering 6, the electro isolating lock 7 the potential leading-out wire 8

Using the liquid-metal measuring electrode allows to create the tool for precise monitoring and effective means for varying the RedOx–potential of molten salts in the electrochemical cell of the following kind [8]

$$Mo \mid Na \mmid\mid Na^+ – \beta''–Al_2O_3 \mid\mid Mo \mid Pb[Na] \mid salt\ [Na], \qquad (3)$$

when the measuring electrode "Pb[Na]" is organized so that the thermodynamic activity of sodium in it coincides with its activity in the salt. One can easily provide that if he uses a thin layer of liquid lead between the solid electrolyte and the salt (for example, in a capillary-porous structure of metal or carbon fiber) or in a direct-contact heat and mass exchanger "lead/salt".

The principle of operation of such gauge is based upon the e.m.f. measurement in the electrochemical cell (3) by high-resistance voltmeter. The liquid-metal electrode 1 (measuring) directly contacts the molten salt and exchanges with it by atoms of sodium providing the thermodynamic equilibrium and protecting the solid electrolyte 2 from liquid-salt corrosion. E (2) of the sodium gauge is determined by its thermodynamic activity, a_{Na}, in liquid lead and accordingly in the molten salt because they are in thermodynamic equilibrium on sodium. It is easily achieved due to high diffusion mobility of sodium atoms in the molten salt and liquid metal.

IV. DISCUSSION OF RESULTS

The gauge of sodium (lithium) thermodynamic activity is possibly used also as the reversible pump of sodium (lithium) atoms in the liquid salt. Indeed, a little positive (or negative) over voltage in the cell (3) will lead to the transfer of alkali cations from the reference electrode 3 to the measuring electrode 1 and forward to the molten salt (and vice versa) due to their thermodynamic equilibrium on the alkali metal.

Thus, it is possible to regulate RedOx–potential of molten salt and to support it at any level with high accuracy (±5 mV).

Theoretically, the management of RedOx–potential of the salt fuel composition and simultaneously as a coolant should be provided loop wide and online in MSR. However the control of this parameter can be organized in the most hazardous point of the loop – in the hot side where the greatest corrosion of structural materials and the strongest change of molten-salt RedOx–potential are expected due to the intensive mixing of the coolant in the loop.

It is possible to find also a range of allowable values of the RedOx–potential in the salt coolant and carry out experiments on verification of this model. Then, the choice of a required control point in the loop will be dictated by adequacy of obtained results to a real state of circulating system as a whole. At the same time, a source of direct and return titration of basic metal in the molten salt can be installed in other point of the loop. It is important to provide the control the RedOx–potential so as to hold the given quality of the coolant, to minimize the rate of corrosion of structural materials in the entire loop and to guarantee an effective extraction of impurities from the MSR fuel composition. Thus, the issue for effective extraction of actinides and lanthanides separately without the addition of basic metal becomes dominant.

V. CONCLUSIONS

The maintenance with high accuracy on the given level of the RedOx–potential of MSR fuel composition at continuous and precise monitoring this parameter in the first loop is the key factor of a molten-salt technology. For this, it is necessary to develop the electrochemical gauge of thermodynamic activity of sodium (lithium) in the molten salt upon the base of solid electrolyte, $Na^+ (Li^+)–\beta''–Al_2O_3$. In this case, it is possible to provide precise measurements of RedOx–potential of molten salts in excluding the direct contact of aggressive molten salt and solid electrolyte by thin layer of neutral liquid metal, for example, lead.

The necessity of such development is caused by poor identification of transition $M^{(n+1)+} \leftrightarrow M^{n+}$ in all the known voltammograms that reflect common fault for current measuring technique: the strong polarization of electrodes. It can become so large that the basic-metal components of molten salt can be removed alongside with the disproportion of impurities.

For effective using molten salts as MSR fuel compositions and coolants as well as a pyrochemical medium for reprocessing of a spent fuel, the precise control

and fine varying the RedOx–potential liquid salt is required because a small over voltage (~10 mV) is allowable for cathode reducing dissolved at effective dividing of elements in molten salts. It is possible only if one can divide methodologically incompatible problems of the metal reduction and varying the RedOx–potential of molten salt: the electrochemical reduction is to be carried out at the minimal over voltage, and the preparation of salt solution for the given level of reduction potential is to be carried out by fine titration of basic metal, for example, sodium or lithium.

ACKNOWLEDGMENT

REFERENCES

[1] *MSR Program Semiann. Progr. Rept.* Feb. 29, 1968, ORNL-4254.

[2] V. M. Smirnov, *Electrode Potentials in Molten Chlorides*. Moscow, Russia: Science, 1973.

[3] A. I. Gusev and A. A. Rempel, *Structural phase transitions in non-stoichiometric compounds*. Moscow, Russia: Science, 1988.

[4] P. N. Alekseev and A. L. Shimkevich, "On voltage-sensitive managing the RedOx–potential of MSR fuel composition," in *Proc. ICONE16*, 2008, paper ICONE16-48176.

[5] P. N. Alekseev et al, "Theoretical and experimental studying a high-flux molten-salt reactor" in Proc. *13th Russian conference on physical chemistry and electrochemistry of the molten scoria and solid electrolytes*, 2004, pp. 134-137.

[6] H. Boussier et al, *The European pyro-metallurgical processing research program PYROREP*: main issues. Report # FIKW-CT-2000-00049 (Project # FIS5-1999-00199), October 2003.

[7] A. L. Shimkevich, "Diffusive polarization of electrodes in molten-salt galvanic circuit," in *Proc. ICONE20*, 2012, paper ICONE20-54633.

[8] P. N. Alekseev, E. I. Grishanin, and A. L. Shimkevich, "The sodium gauge for measuring RedOx-potential of molten salts," RF Patent 2012102126, Jan. 24, 2012.

Pavel N. Alekseev was born on March 3, 1949 in Rostov region, Russia. He has began scientific activity in Department of Theoretical and Experimental Physics of Nuclear Reactors of Moscow Engineering and Physics Institute (MEPhI) in studying perturbation theory and numerical methods for calculating nuclear reactors and teacher's job as head practice and degree designing of students in a post of the trainee researcher from the moment of the termination of MEPhI in 1972.

From 1974 to 1977, being trained in postgraduate course of MEPhI, he investigated methods of the perturbation theory under the codes created by him of the characteristic of fast and thermal reactors and critical assemblies. Since June 1977 after the successful termination of a post graduate course on distribution constantly works in NRC "Kurchatov Institute"he has protected the Ph.D. thesis "Finite-difference iterative methods and the perturbation theory in calculation researches of nuclear reactors."

In 1988 he read a rate of lectures "Nuclear reactors of new generation" to students 5 rates MEPhI. Constantly he carries out as a scientific adviser of post-graduate students. Under his scientific advice six PhD thesis are successfully protected. Now he is the supervisor of studies of two post-graduate students and the co-author of books: "Nuclear Reactors of the Increased Safety" and "Nuclear Energy. Expert ratings of development" Dr. Pavel N Alekseev is the known expert in the field of physics and safety of future nuclear reactors. He is the organizer of new scientific researches in designing an optimum structure of Russian nuclear-power complexes. In 2011, he participated in development "Strategy of development of nuclear power of Russia till 2050". He is switched to structure of scientific councils NRC KI, enters into advisory council of STC NRS on certification of software. He is the co-author more than 160 scientific publications and 18 inventions. Rosatom from Russia nominates him in structure of Expert group of the international project Generation 4 (GIF). A number of scientific works on innovative reactors and nuclear fuel cycle in support of the researches conducting in IAEA within the framework of international project INPRO is issued under his scientific advice.

Alexander L. Shimkevich was born on February 1, 1947 in Budapest, Hungary. He received the M.S. degree in nuclear physics from Physics and Technology Institute (PhysTech) in Moscow, Russia; PhD degree in nuclear power units from Institute for Physics and Power Engineering (IPPE) in Obninsk (Russia); and D.S. degree in thermal and molecular physics from High Temperature Institute of Russian Academy of Sciences (Moscow). He has been employed by IPPE in 1971 as Jr. Researcher, Senior Researcher (from 1986), and Head of Laboratory (from 1993). From 2002, National Research Center "Kurchatov Institute" has employed him as the Head of Laboratory, Head of Department (from 2007), and Head of Division now.

Dr. Shimkevich had about forty years of R&D experience in condensed matter theory for application to liquid metal technology for NPP, designing a nuclear fuel in solid and liquid states. He is one of the principals who developed unique low-temperature oxygen and hydrogen sensors based upon solid oxide electrolytes. His areas of expertise include statistical estimation systems and information technologies, theory for inhomogeneous solids and melts and their purification technology, electrochemical systems and solid-electrolyte devices, liquid-coolant technology for nuclear power units and designing reactor materials in a whole.

Prof. Shimkevich is the author of monograph "The composition principles for designing nuclear-reactor materials" and has co-authored over 170 scientific publications (preprints, reviews, papers, and patents) in various areas of basic and applied physics, applied mathematics and simulation, statistical and structural analysis, electrical and physical chemistry. He has developed fluctuation theory for inhomogeneous melts as a consequence of the first-order component phase transitions.